

# **Water-Soluble Metal-Binding Polymers with Ultrafiltration**

## **A Technology for the Removal, Concentration, and Recovery of Metal Ions from Aqueous Streams**

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The use of water-soluble metal-binding polymers coupled with ultrafiltration (UF) is a technology under development to selectively concentrate and recover valuable or regulated metal-ions from dilute process or waste waters. The polymers have a sufficiently large molecular size that they can be separated and concentrated using commercially available UF technology. The polymers can then be reused by changing the solution conditions to release the metal-ions, which are recovered in a concentrated form for recycle or disposal. Pilot-scale demonstrations have been completed for a variety of waste streams containing low concentrations of metal ions including electroplating wastes (zinc and nickel) and nuclear waste streams (plutonium and americium). Many other potential commercial applications exist including remediation of contaminated solids. An overview of both the pilot-scale demonstrated applications and small scale testing of this technology are presented.

Regulatory limits for discharge of radioactive metal-ions from the United States Department of Energy (DOE) nuclear facilities have become markedly lower in recent years, and older technologies for treatment of waste streams such as carrier precipitation have become much less efficient from an overall systems engineering perspective. In the late 1980s our separations team at Los Alamos National Laboratory began evaluating the use of water-soluble metal-binding polymers in combination with UF as a more cost-effective way of meeting the increasingly stringent regulatory requirements for removal of actinides from waste waters.

The concept of using water-soluble metal-binding polymers with UF as a process was first proposed in the late 1960s by Michaels (1). Relevant actinide work had been done by Bayer and Geckeler (2) who, in collaboration with Myasoedov's group (3), tested actinide binding with a water-soluble metal-binding polymer containing the 8-hydroxyquinoline ligand. We tested the concept with the same laboratory-prepared polymer along with a number of other commercially available polymers (4) and found that though some polymers did indeed

concentrate americium (III) and plutonium (III)/(IV) (the major alpha-active contaminants in our waste waters), our goal of reaching ultra-low discharge levels could not be met with these polymer systems.

Consequently, we began designing polymers that would have higher binding constants for the actinides, particularly americium and plutonium, and would have overall better physical properties for use in the UF process. This approach coincided with the development in our laboratory of rapid survey techniques for evaluation of new polymers. The concept was developed into a preconcentration procedure for analysis of actinides in very dilute solutions (5). From the analytical scale the process evolved to the bench- and pilot-scale for actinide waste water treatment.

Shortly after our work with actinides began, we had the opportunity to collaborate with the Boeing Space and Defense Group, Seattle, WA, on a joint project for electroplating waste minimization. A key issue for the electroplating industry was the removal of valuable or hazardous metal-ions from dilute waste streams without generating sludge that requires disposal in landfills. The goal became recycling in a near-closed loop process. After considering a number of technologies in a best available technology review (6), it was decided that watersoluble metal-binding polymers with UF had the potential to meet the needed goals of this project for dilute rinse water treatment and metal-ion recycling. From the analytical-scale studies a process was developed and taken to the bench and pilot scale for an electroplating rinse water recycling process (7). The first metal recovery systems targeted for commercialization for the electroplating industry were nickel (bright nickel, nickel strike), zinc, copper (copper strike), zinc/nickel alloy, and nickel-tungsten alloy (8).

The need in the electroplating and the nuclear industries for the recovery and removal of metals that exist as oxyanions has led to many studies using watersoluble polymers for the removal of a variety of oxyanions. These oxyanions include chromate, tungstate, molybdate, selenate, arsenate, and pertechnetate. The removal of some oxyanions from aqueous solutions using water-soluble metalbinding polymers with UF has been reported (9).

A logical extension of this technology, once it became commercially available, was further evaluation for removal and recovery applications for other transition and main-group metals (toxic, valuable, or nuisance) from other aqueous process and waste solutions such as acid mine drainage (10) and from solid surfaces. We have been studying the separations chemistry of the elements highlighted in periodic chart format in Figure 1.

Periodic Table of the Elements																					
H																	He				
Li	Be															B	C	N	O	F	Ne
Na	Mg															Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr				
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe				
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn				
Fr	Ra	Ac																			
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu					
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr					

Elements under investigation for recovery/  
removal using Polymer Filtration

**Figure 1.** A Periodic Table Summarizing Elements Under Study for Application of Polymer Filtration Technology.

## The Concept of Water-Soluble Metal-Binding Polymers with UF (Polymer Filtration)

Polymer Filtration (PF) technology uses water-soluble polymers prepared with chelating or ion-exchange sites to sequester metal-ions in dilute aqueous solutions. The water-soluble polymers have a sufficiently large molecular size that they can be separated and concentrated using commercial UF technology. Water and smaller unbound components of the solution pass freely through the UF membrane allowing for the concentration of the polymer/metal complex. By adjusting the solution conditions, the metal-ions are released and are recovered in a concentrated form for recycling or disposal using a diafiltration process. The water-soluble polymer can be regenerated for further waste-stream processing.

The relative efficiency with which an UF membrane retains or rejects a metal species can be determined experimentally with each species assigned a numerical value between 0 and 1 called the rejection coefficient ( $\sigma$ ). A rejection coefficient of 0 means that the species freely passes through an UF membrane (permeate) while species with a rejection coefficient of 1 are completely retained (retentate). Small metal-ions will pass freely through the membrane ( $\sigma = 0$ ) unless the effective size is temporarily increased by binding to the polymer ( $\sigma < 1$ ). In the case of a polymer/metal-ion complex in which the polymer (P) is physically too large to pass through the UF membrane, the rejection coefficient of the metal-ions ( $Mn^{+}$ ) in the presence of a complexing polymer (P) is a reflection of the equilibrium or stability constant ( $K_s$ ) of the complex, which is a measure of the affinity of the polymer for a metal-ion.



$$K_s = \frac{[PM^{n+}]}{[P][M^{n+}]} \quad (2)$$

**Concentration Mode.** Generally, there are two modes of operation in PF (11). The first is the concentration mode, schematically shown in Figure 2, where the volume in the retentate is reduced by simple UF. The final concentration of any species in solution can be determined by:

$$C_f = C_0 \cdot \left( \frac{V_0}{V_f} \right)^\sigma \quad (3)$$

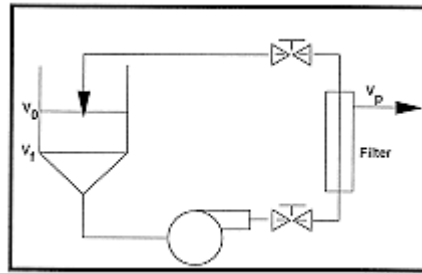
where  $C_f$  is the final concentration of the species,  $C_0$  the initial concentration,  $V_0$  the initial volume of solution,  $V_f$  the final volume, and  $V_p$  the permeate volume. If the rejection coefficient of the species is 1, as would be the case for the water-soluble metal-binding polymers, then equation 3 simplifies to:

$$C_f = C_0 \frac{V_0}{V_f} \quad (4)$$

For two species in solution, a polymeric/metal-ion species (PM) and a molecular impurity (A), where  $\sigma_{PM} \gg \sigma_A$ , the UF of the solution should result in the concentration and enrichment of P based on:

$$\left( \frac{C_A}{C_{PM}} \right)_f = \left( \frac{C_A}{C_{PM}} \right)_0 \cdot \left( \frac{V_0}{V_f} \right)^{-(\sigma_A - \sigma_{PM})} \quad (5)$$

UF is the basis for a significant degree of purification during concentration of polymer/metal-ion complexes in solution.



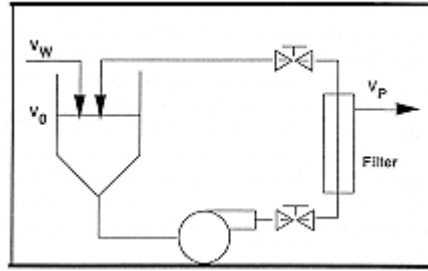
**Figure 2.** Schematic of Concentration Process by UF

**Diafiltration Mode.** The second mode of operation in PF is diafiltration (see Figure 3). Wash water ( $V_w$ ) is added to the retentate at the same rate that the permeate is generated so as to maintain a constant retentate volume. In the

diafiltration mode, the lower molecular weight species in solution are removed at a maximum rate when the rejection coefficient equals 0. The retentate is, in effect, washed free of smaller solute. Theoretically, the percent solute (any dissolved species) remaining in the retentate can be calculated by using equation 6:

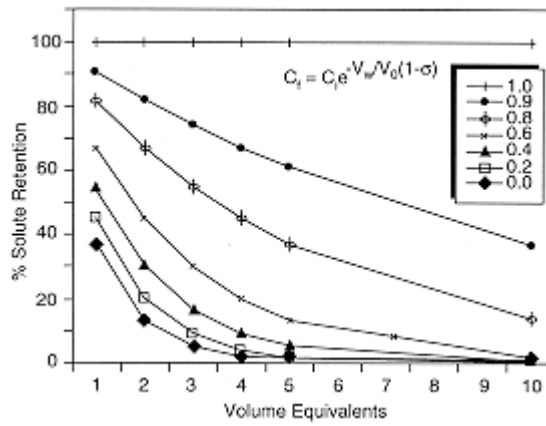
$$C_f = C_0 \cdot e^{-\frac{V_w}{V_0}(1-\sigma)} \quad (6)$$

where  $V_w$  is the volume of solute free liquid (volume-equivalents) added, which also equals the amount of permeate produced ( $V_p$ ).



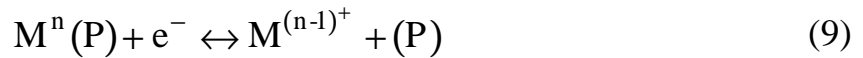
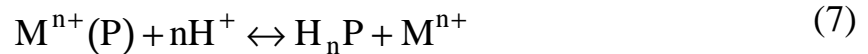
**Figure 3.** Schematic of the Diafiltration Process

The effects of various rejection coefficients on the percent solute retained during a diafiltration process are shown in Figure 4. It can be seen that theoretically, after 5 volume equivalents of processed solution, >99% of the lower molecular weight species with a rejection coefficient of 0.0 should be removed. Experimentally, however, rejection coefficients of 0.0 are not ordinarily observed. Even weak interactions between the solute and the water-soluble polymer or the UF membrane can yield a small retention value. The curves for low retention coefficients follow an exponential decay with each additional volume equivalent giving diminishing returns in percent solute removed, while higher rejection coefficients approach a linear response to solute removal.



**Figure 4.** Plot of Solute Retained as a Function of Volume Equivalents for Various Rejection Coefficients During Diafiltration

**Methods of Metal Release.** The polymer-bound metal-ion can be released from the polymer by a variety of processes including those shown in the following equations:



where M is the metal-ion, (P) is the water-soluble polymer, L is a competing molecular complexant, n is the oxidation state of the metal-ion, and the reduction reaction can be either chemically or electrically driven. When the metal is released by a proton (equation 7) or by a complexant (equation 8), the polymer-free metal-ion is recovered by a diafiltration process. In some unusual instances, the metal-ion may be so tightly bound to the polymer that destruction of the polymer (incineration, hot acid digestion, smelting, etc.) is required to recover the metal. Optionally, for waste management purposes it may be most economic to solidify the polymer-bound metal, for example, in a grout or cement material, such that it passes Environmental Protection Agency (EPA) Toxicity Characteristic Leaching Procedure (TCLP).

**General Process Conditions.** Generally, the concentration range for the water-soluble polymer in solution ranges from 0.001 weight/volume percent to 20 weight/volume percent of final concentrated solution. It is sufficient, and in some cases desirable, to have only enough polymer in solution such that the polymer's metal-ion loading approaches 90 to 100%. Using higher concentrations of the watersoluble polymer will result in lower flux rates through the membrane during

the concentration stage. The use of a high initial polymer concentration can sometimes cause aggregation of the polymer and reduced metal-ion binding capability. In this case, operation at lower initial polymer concentrations can allow more complete metal binding and the polymer can then be concentrated to higher final concentrations with overall improved performance.

During the concentration stage for analytical applications, the polymer and metal-loaded polymer concentration can often become quite high and, in the case where the solution goes to near dryness, it can approach 90% of the weight of the concentrate. For a semi-continuous process it is necessary to work at low polymer concentrations to maintain high permeate flux across the membrane during the concentration stage of the process. During the diafiltration stage the polymer concentrations will always be higher, but at this juncture the volumes being treated are small. The flux is dependent on the transmembrane pressure which is commonly in the range of 25 to 50 psi. However, the increase in flux with transmembrane pressure is limited by concentration polarization and the flux gains are often small beyond 50 psi for typical tangential-flow, hollow-fiber UF units (11).

**Polymer Leakage Through the Membrane.** Ideally, there is no polymer permeating through the UF membrane. If there is any polymer breakthrough ( $\sigma < 1.0$ ), it will ultimately be lost from the system (12). This result is unacceptable from a number of process perspectives. First, the polymer must remain in the system to maintain its working concentration. Second, polymer contamination in the permeate can create further problems downstream. Third, loss of metal-loaded polymer that would carry bound metal-ions into the permeate can result in failure to achieve target discharge limits. If there were only 1 ppm loss of polymer from a system that contains 1000 ppm polymer (which might be environmentally acceptable), a 50% loss of material in approximately a million volume equivalents would occur. At ~2% polymer breakthrough, as has been reported for one experimental system (13), 50% polymer loss would occur in approximately 35 volume equivalents. This amount of polymer loss is unacceptable for a viable process.

Measurement of polymer breakthrough has required the use of a variety of methods because each polymer has different functional groups that require different techniques to determine their presence in low concentration. For example, we have used UV-Vis absorption spectra of highly colored metal-ion complexes and total organic carbon analysis to detect polymer in the permeate. However, the absorption spectra are generally limited to levels of 1 ppm or higher and the presence of other organic compounds in the feed solution can interfere with the carbon analysis.

We are developing tags for the polymer backbones that will detect breakthrough at the ppb level or less and will be useful for a wide variety of polymers.

**Concentration Factors and Low Level Metal Ion Removal.** When the goal of a process involves the removal of metal-ions to very low levels, it can be useful to think in terms of the resulting metal-ion concentration in the permeate solution as opposed to percent metal-ion retained in the retentate. At 99% retention of metal-ions from a solution with an initial concentration of 1000 ppm, 10 ppm remain in the permeate. For most RCRA or toxic metals this amount still represents an unacceptable discharge level and the resulting aqueous stream could not be discharged to any Publicly Owned Treatment Works (POTW). In aqueous streams containing radioactive metal-ions the decontamination factors must often be even greater. A solution containing  $1 \times 10^6$  pCi/L of plutonium-239 will require 99.999% removal to reach 10 pCi/L. Thus, in evaluating a process it may be more practical to take into account the final waste stream concentration than to consider the percent of metal removed.

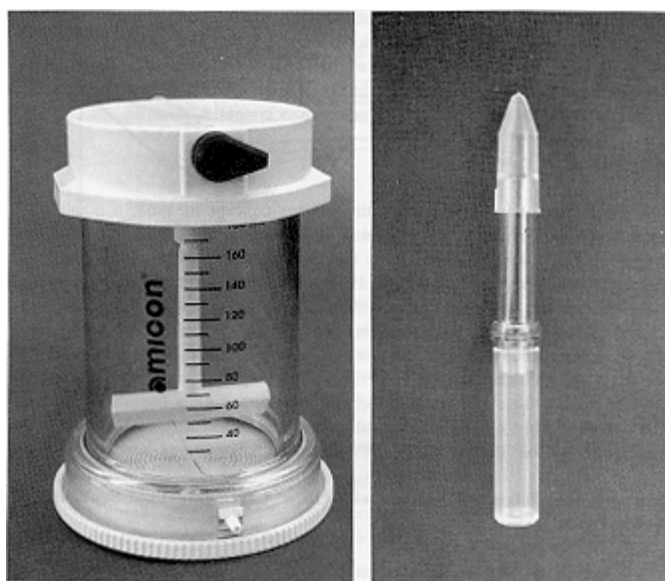
Calculation of a concentration factor (CF) for a PF process cycle will require knowledge of the process system which includes: the initial feed metal-ion concentration and volume, the final metal-ion concentration and volume, the size of the reactor, and the initial polymer concentration (12). The polymer concentrations do not exceed 20% in a continuous process because of the reduction in flux rates. Thus, if the reactor size is 20 L (this includes the holdup volume of the system) and the initial polymer concentration is 1% w/v, we can concentrate the reactor volume from 20 L to 1 L at the end of the concentration phase. If the metal-ion concentration in the feed going to the reactor is 100 ppm (e.g., Cu, AW 63.5) and a 1% w/v polymer solution has a capacity of 0.25 g Cu per g of polymer and a 20 L reactor has 200 g of polymer, we can bind 50 g of copper which represents 500 L of feed. Thus, the concentration of 500 L to 1 L is a CF of 500 ( $CF = V_0/V_f$ ).

The majority of this process will thus be run at a polymer concentration of 1% w/v or less to maintain the high flux rates. Only at the end of the batch will flux rates be reduced substantially as the polymer concentration is increased from 1 to 20% w/v. In actual single-stage practice <100% of the polymer capacity is used to avoid metal-ion breakthrough that would exceed the discharge limit. When the metalion is released from the polymer by diafiltration it will take three volume equivalents (one liter is one volume equivalent in this case) or three liters to collect 95% of the metal. Thus the actual CF will be  $500/3 = 166$ .

If the feed metal-ion concentration were ten times less, then the CF would be 10 times greater, or  $5000/3 = 1666$ . For very dilute metal-ion solutions the CF value can be very large.



**Rapid Survey Techniques of New Polymers.** Various UF equipment has been used to evaluate a polymer's ability to both bind and release selected metal-ions. The most common benchscale units are stirred cells (3). These units are driven by gas pressure and are too laborious and time consuming to assemble for rapid survey of large numbers of polymers under a variety of reaction conditions. We have adapted centrifugation driven UF units developed for protein purification to a rapid survey technique of our polymers under various conditions (5). These units are commercially available through companies such as Amicon, Fisher, Millipore, etc. They use both a dead-end filtration as in the Centricon-10 units (Amicon) and a reverse dead-end for the Centraprep units (Amicon) and have sample volumes from 0.5 to 20 mL. Photos of both a stirred cell (200 mL volume) and of a Centricon-10 (2 mL volume) unit appear in Figure 5. The membranes we use typically have a molecular weight cut off(MWCO) of 10,000 to 100,000 Daltons and are composed of a variety of membrane materials such as cellulose acetate, polysulfone, and fluoropolymers.

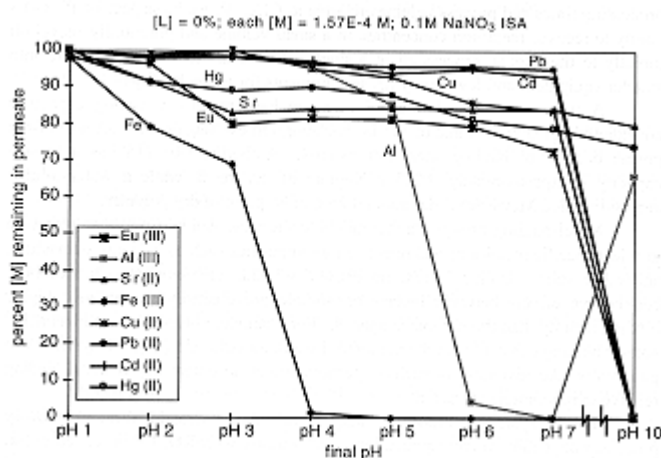


**Figure 5.** Two Hundred mL Stirred Cell (left)  
and a two mL Centricon-10 unit (right)

These small centrifugal units are particularly useful for waste minimization purposes when evaluating polymers for actinides and other radionuclide separations because of the small amount of sample required for testing and because there are no transfer losses. Both the top and the bottom compartments of the unit are placed in separate scintillation vials and the whole unit can be measured (4, 5). The data is usually reported as ppm metal or pCi/L remaining in the permeate as a function of the particular parameter being tested. Data for actinide removal is often reported as distribution coefficients (D) as a function of

the parameter under study. The D value calculation was adapted from the D determinations for ion exchange resins where  $D = (\text{Total Bound Metal} / \text{Total Unbound Metal}) \times \text{Phase Ratio}$ , where the Phase Ratio is (Initial Solution Volume in mL / Initial Polymer Weight in gm). Since this equation includes a phase ratio and very small amounts of soluble polymer can have large effects, we can realize some very large D values. For example, a 0.1% w/v polymer solution that retains 99% of a metal-ion gives a log D value of 5.0.

Blank measurements performed in the absence of polymer to determine the behavior of the metal-ion under the experimental conditions used can be useful information. With metals that form hydroxide precipitates or other polymeric inorganic species under the solution conditions, it can be difficult to sort out which species are being removed in the UF step. The presence of the polymer can influence these reactions in a variety of ways. The complexing functionality on the polymer can suppress precipitation reactions, but water-soluble polymers are also commonly used as flocculation agents. Clearly, the order and timing of reagent addition can be crucial to the PF process. Figure 6 gives an example of results of UF with a 10,000 MWCO ultrafilter for a number of divalent and trivalent metal-ions after addition of base to an acid solution in the absence of polymer. An UF operation on a solution of this composition using a polymer that was very selective for Hg(II) at pH 4 would remove most of the Fe(III) as a precipitate. Hydrolyzed metal-ions can bind with the polymer, but their presence in solution influences the binding constants as with any metal/ligand complex system.



**Figure 6.** Plot of % Metal Ions Remaining in Solution after UF as a Function of pH in the Absence of Water-Soluble Polymer

## Past Versions of Polymer Filtration

After Michaels' (1) first proposal of the process concept in 1968, a number of researchers have developed and evaluated the concept under a variety of process

names. French researchers worked on the concept in the early 1970s (14). A Japanese patent was issued in the late 1970s (15) and a German team, Bayer and Geckeler, reported their work in the 1980s (3), calling the process Liquid-Phase Polymer-Based Retention. An American team reported work in the early 1990s (13) and called the technology Polyelectrolyte-Enhanced UF. An excellent review article by Geckeler and Volchek appeared in 1996 (16) which gives the current status of the technology from those authors' perspective. We started using the name Polymer Filtration (PF) when our commercialization activities began as the previous terms were considered too cumbersome by our industrial collaborators (17).

## **Comparison of Polymer Filtration with Other Commonly Used Separations Technologies**

PF is a technology for the concentration, removal, and recovery of metal-ions from dilute aqueous solutions. In general, we have applied this technology to feed concentrations of  $< 1000$  ppm metal content. Though higher metal-ion concentrations can be treated, the concentration factors become small. Other processes for metal removal/recovery from dilute solutions include Precipitation (PPT), biphasic Liquid-Liquid EXtraction (LLEX), Ion eXchange (IX), Chelating Ion eXchange (CIX), Reverse Osmosis (RO), Evaporation (EV), filtration (carbon, sand, etc.), ElectroDeposition (ED), and ElectroRecovery (ER). Aqueous chelating ion exchange is the technology most closely aligned with PF because the metal-ion binding chemistry is similar and the chelators can have high metal-ion selectivity. LLEX can also employ very selective chelators, but uses two immiscible liquid phases rather than a solid and liquid phase as in CIX.

Binding kinetics are very rapid with PF because of the homogeneity of the system. With CIX phase transfer between the aqueous solution and the solid resin must occur. This process can be relatively slow in both the metal uptake and release. For example, 90% loading can be attained in PF within seconds, while it may require hours to attain the same level of loading with some resins. This difference makes the kinetics of PF in the range of 104 times faster than CIX. Thus, in CIX, column flow rates and column material amounts have to be optimized to allow for slower metal binding and release, and the amount of regeneration solution required to recover the metal-ions can be large. PF can significantly reduce processing times and process volumes relative to CIX. A useful aspect of PF is its ability to recover metal-ion concentrate in a small volume and potentially recycle it directly to the original process all in a single unit. This ability can translate into smaller equipment and fewer polymer requirements for PF technology.

A water-soluble chelating polymer can have metal-ion loading capacities considerably greater than that of similar chelating ion exchange resins because of the greater density of binding sites. For example, Amberlite IRC-718 has a loading capacity of approximately 0.025 g Ni/gram of dry resin, while a water-soluble analogue called Metal-Set-Z has about 0.25 g of Ni/gram of dry polymer.

Metal-binding groups can be built into the water-soluble polymer structure to select specific metal-ions and reject benign impurities such as calcium, potassium, and other salts. Unlike LLEX, no organic solvents are required. In addition, cooperative effects between ligands on soluble polyelectrolytes can give higher binding affinity than the monomer ligands. For example, polyacrylic acid has a  $10^4$  greater binding constant than the monomer ligand, glutaric acid (18). PF systems can potentially take advantage of such cooperative effects to obtain higher metal binding relative to monomeric extractants.

The PF system can have advantages over other conventional metal recovery processes depending on the application. By contrast with RO, PF is carried out at low pressure (commonly  $< 25$  psi). PF is a relatively low energy process compared to EV and will not damage heat-sensitive solutes. RO and EV, as compared to PF, are unselective processes for solutes, concentrating all waste stream salts and materials, including metal-ions that may be impurities. PPT is often unspecific, generates large amounts of secondary waste, and is limited by solubility products. PF functions well, perhaps even better, at low metal-ion concentration (19), whereas some technologies like PPT have limited applicability. ED can recover metal-ions selectively as pure solids, but not as ions in solution. This process does not allow for efficient recycling in some applications. ED/ER tends to be inefficient at low metal-ion concentrations. The choice of a particular technology is dictated by the required end result and the total system cost. For dilute solution and waste polishing requirements, PF is a cost-effective option.

A very useful aspect of PF is the possibility of developing formulations (mixtures) of polymers with different chelators to recover suites of metal-ions and of separating the concentrated metal-ions from each other with different stripping chemistry. The polymers can also lend themselves to having multiple ligand groups on one polymer. We have over 30 different polymers under development with a variety of functionalities and many polymeric structures are already reported in the literature (16). The applications described in more detail below use water-soluble polymers reported in the literature as well as some new proprietary formulations.

The combination of concentration and diafiltration UF processes provides an effective method for the recovery, concentration, and purification of metal-ions in solution. Permeate streams 'free' (in a regulatory sense) of hazardous metal-ions

will result. A number of industries successfully use simple UF processes for various applications, including water purification, waste treatment, pharmaceuticals, and the food and beverage industries. Consequently, UF is an accepted technology in industry.

## **Process Applications**

We have been able to apply PF successfully to a variety of actual waste streams and have been involved with the commercialization of the technology for certain applications by working closely with industry. Further research and development work is ongoing for additional applications. The following paragraphs describe some of the developments leading toward commercialization.

**Actinide Removal from Aqueous Streams.** Because of the nature of LANL's mission and our involvement in actinide separations work for many years, our first application developed for PF has been in the area of ultra-low level analysis of actinides and removal of actinides from process and waste streams.

**Development of an Analytical Procedure for Preconcentration of Actinides.** The analysis of trace elements in environmental and industrial processes has become very important. Though modern instrumentation can measure increasingly lower concentrations, elements are often still present at levels near or below the detection limit. Routine radiochemical counting methods and inductively coupled plasma-mass spectrometry (ICP-MS) cannot easily measure directly such concentration levels as low as 30 pCi/L (1.1 Bq/L) total alpha, the new DOE Derived Concentration Guideline (DCG) for process waters containing alpha-emitting radionuclides or the 0.05 pCi/L limit for americium or plutonium in groundwaters near the Rocky Flats site in Colorado. Analyses can be further complicated by high concentrations of alkali and alkaline earth salts and silicates in waste waters. These ions may interfere with the analysis, making preconcentration of samples by evaporation ineffective. This has necessitated the development of rapid, reliable, and robust analytical techniques for measuring low concentrations of actinide ions.

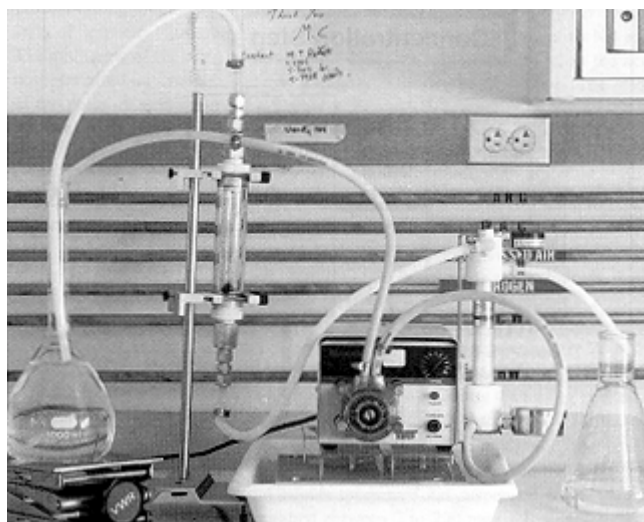
PF had been shown to be useful in preconcentrating actinide ions from aqueous systems by Bayer and co-workers (3). We have been able to use water soluble metal-binding polymers combined with UF as an effective method for selectively removing dilute actinide ions from high salt solutions on an analytical scale (4,5). For some of the preliminary studies we used a waste water simulant that is typical of the Radioactive Liquid Waste Water Treatment Facility (RLWTF, TA50) (Technical Area 50) at LANL (4). Development studies were performed using <sup>241</sup>Am spiked simulants to determine polymer formulation, binding conditions, and accountability before we addressed actual waste waters. It

was found that working at pH 4 gave the best accountability as it minimized adsorption of actinides to the surface of the apparatus. The need for working at lower pH values required the development of new polymers that functioned well in this range (3,4,5).

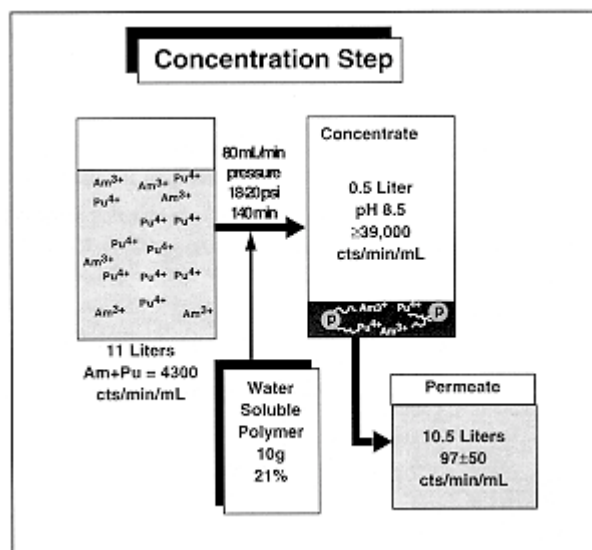
After substantial polymer and methods development (5) we were able to concentrate by PF one liter of actual waste water from the RLWTF and compare that with 0.1 liter of the same waste water preconcentrated by evaporation (there were so many solids that we could only evaporate 100 mL to 1 mL). The results indicated 318 (duplicate 314) cpm/L gamma activity in the waste water treated by PF and 310 cpm/L in the normalized evaporated solution. Although we used direct gamma counting techniques for this test, it was possible to use other measurement techniques such as ICP-MS, alpha scintillation spectroscopy, or alpha plate counting. Sample preparation for other modes of analysis was accomplished by quantitatively dissolving the cellulose acetate UF membrane with its polymer filter cake in sulfuric acid (5).

**Bench-Scale/Glovebox Studies for Actinide Removal from Plutonium Facility Distillate Waters.** The results from the analytical application were so encouraging that it was decided to determine if this method could be developed into a process application. There are a number of facilities at LANL and other DOE sites where the technology could be applied; for instance, in the Los Alamos Plutonium Facility (TA-55) before the waste water is discharged to the RLWTF. Alternatively, it could be used for waste stream polishing on neutral waters after they reach the RLWTF at TA-50. The discharge limit for the Plutonium Facility acid waste line to the RLWTF is currently  $7 \times 10^7$  dpm/L total alpha (30  $\mu\text{Ci/L}$ ) with typical nitric acid concentrations of 1-6 M. The new discard target in the industrial waste line is  $1 \times 10^6$  dpm/L total alpha (0.5  $\mu\text{Ci/L}$ ) in 0.1 mM nitric acid. Part of this goal will be accomplished by nitric acid recycling from distillation. The target alpha activity from the fractionator is  $10^2$  to  $10^5$  dpm/L total alpha (50-50,000 pCi/L).

We have been performing bench-scale testing to remove alpha activity ( $^{238}\text{Pu}$  and  $^{241}\text{Am}$ ) from distillate waters on two different scales. The first bench-scale testing experiments used a small UF unit with a peristaltic pump similar to that shown in Figure 7. The test results are shown in the flow diagram in Figure 8. In this case we were able to treat 11 liters having 4300 cpm/mL at a flow rate of 80 mL/min to give 10.5 liters of permeate waste water having  $97 \pm 50$  cpm/mL (scintillation counter at 100% efficiency) and 0.5 L of a concentrate with greater than 39,000 cpm/mL. This test met the upper limit of our  $10^5$  dpm/L goal, but also illustrated that if we are to reach the lower goal of  $10^2$  dpm/L (30 pCi/L) that we would need a better polymer formulation and/or two stages of PF.



**Figure 7.** Small UF Unit with a Peristaltic Pump

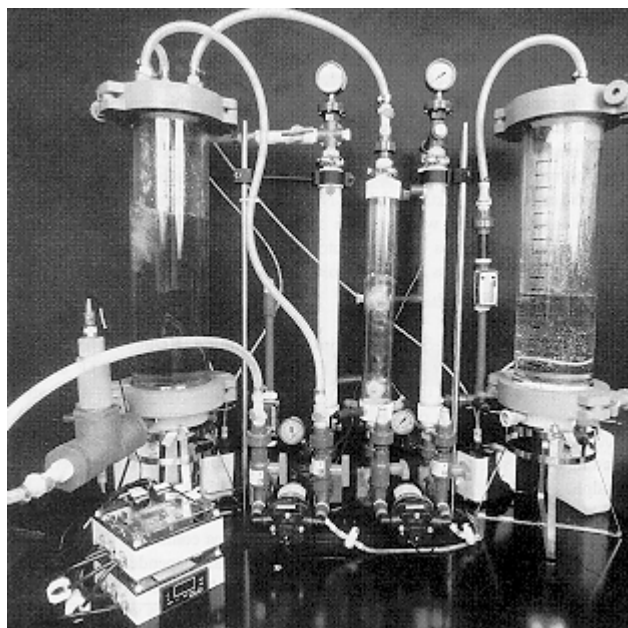


**Figure 8.** Flow Diagram and Results of a Test on Distillate Waters from TA-55

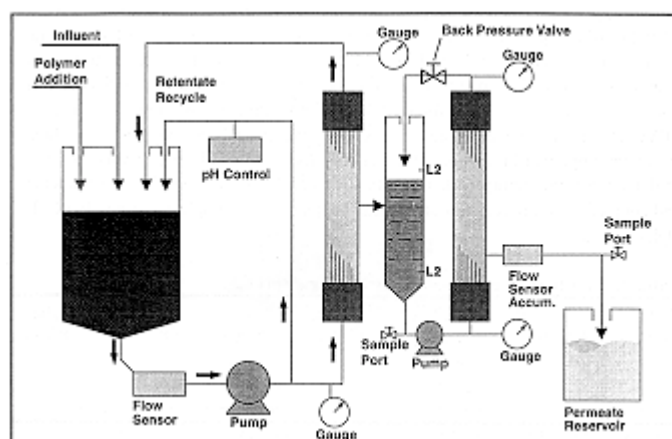
A larger two stage unit was built as shown in Figure 9, having the flow diagram shown in Figure 10. The reservoir holds 10 L and the flux rates were approximately 1 L/min. The pilot-scale unit was initially tested with neodymium(III) nitrate solutions. These Nd solutions are a reasonable surrogate for americium in the process and waste waters. The two stages that we built into the PF unit worked as expected. One gram of polymer (5) was employed in the first 10 L reservoir and 0.1 gram in the second 2 L reservoir. The initial Nd level of 14 ppm was reduced to less than 10 ppb (detection limit for the ICP-AES analysis) in the process during processing of the first 10 L batch which loaded the



polymer to about 20% of "capacity" (assuming a 1:1 mole ratio of the chelating groups to Nd ions). The mole ratio of chelating groups to the Nd(III) ion may be 2:1 or 3:1 in the actual polymer/metal-ion complex and may change with the degree of loading. The loading of the polymer was continued with two additional 10 L batches of Nd solution to observe the expected "breakthrough" of Nd. This work gave us information on the metal-ion capacity of the water-soluble chelating polymer. This unit was placed into a glovebox in the Los Alamos Plutonium Facility and is undergoing further testing with various process and waste solutions, in addition to further optimization of the polymer formulation.



**Figure 9.** Pilot-Scale Two-Stage Polymer Filtration Unit for Installation in a Glovebox.



**Figure 10.** Schematic of Pilot-Scale, Two-Stage Polymer Filtration Process



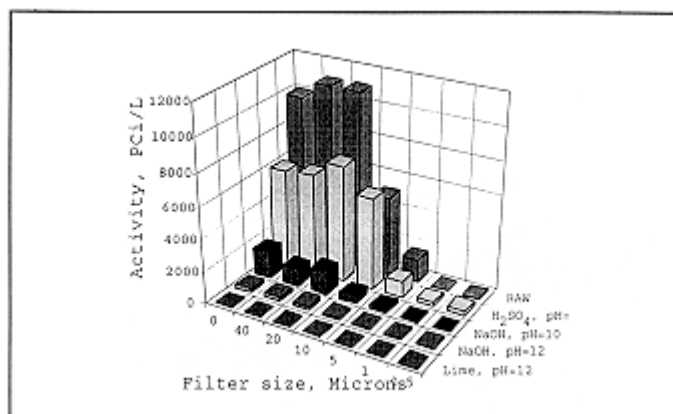
**Bench-Scale/Pilot-Scale Studies for Actinide Removal from LANL Radioactive Liquid Waste Treatment Facility(TA-50).** The RLWTF at LANL receives all the water from the radioactive acid waste lines from many sites around LANL, including that from over 1000 sinks and drains at approximately 20,000 to 30,000 gal/day. The characteristics of the influent waste water can vary dramatically depending on the status of waste generating activities. During the testing period, the total alpha activity of the waste water ranged from 48,800 to 451,500 pCi/L. The vast majority of the alpha activity can be attributed to three nuclides:  $^{241}\text{Am}$ ,  $^{233}\text{Pu}$ , and  $^{239}\text{Pu}$ . Bench-scale testing with ion exchange resins confirmed that these three nuclides exist as both cationic and anionic species. Total suspended solids varied in size with the total quantities measured between 2 to 200 mg/L. It was determined that the split of alpha activity between solid and solution species varied and that the soluble fraction ranged from 1.5 to 5% based on activity levels. Turbidity ranged from 20 to 590 NTU, total organic carbon from 10 to 50 ppm and conductivity from 400 to 1000  $\mu\text{S}/\text{cm}$ . The pH ranged from 3.4 to 9.5.

The waste water is presently treated by an iron/lime precipitation method (20). The problems associated with this method are that the removal of actinides by precipitation generates large volumes of waste sludge, and that LANL is facing new actinide discharge limits that are not readily attainable with the existing precipitation method. Storage of large quantities of low-level waste is expensive and requires constant monitoring, plus these wastes will use a substantial quantity of limited landfill space. The best possible solution to both these problems is to demonstrate a new process for removal of actinides without generating large secondary waste streams.

From previous experiments we have shown that a large percentage of the alpha activity could be removed by simple micro-filtration techniques as shown in Figure 11. Though this technique provides substantial alpha activity removal, it does not consistently meet the new discharge level requirements of 30 pCi/L. To meet this low level, we have proposed prefiltration of the waste water to remove the particulate fraction and then treatment of the filtrate with the PF process to polish to the required levels. Another approach would be to add the water-soluble polymer to the waste stream and remove all alpha activity simultaneously by UF of suspended solids and the water-soluble polymer-bound metals. Both approaches have been tested.

Experiments were performed on a number of different days at the TA-50 TILWTF using equipment similar to that displayed in Figure 7. Table I shows the influent

alpha activity followed by the results of several different treatment approaches. The first treatment used a small amount of Betz 1175 flocculating polymer followed by a 5  $\mu\text{m}$  filter. The second treatment was simple UF (10,000 MWCO) which removed more activity than the flocculated system. The final treatment employed PF and gave the best results, <100 pCi/L, which was the limit of detection from facility background (evaporated 10 mL of sample on a planchet and counted). Controlled laboratory measurement of one sample showed < 30 pCi/L alpha per nuclide.



**Figure 11.** Results of a Filtration Study Using Different Filter Sizes and Different Waste Treatments to Determine the Amount Of Activity Removed by Simple Filtration

**Table I.** Test Results on TA-50 Waste Water at pH 6.5

<i>Run Date</i>	<i>Net Alpha Activity (pCi/L)</i>	<i>Rough Bag Filter, 5<math>\mu\text{m}</math> Pretreat Betz 1175 (pCi/L)</i>	<i>UF (pCi/L)</i>	<i>PF 100 ppm Polymer (pCi/L) In Plant</i>	<i>238Pu (pCi/L)</i>	<i>241Am (pCi/L)</i>
3/26/96	451,552	3,737	3080	< 100		
3/27/96	218,550	17,180	5,000	< 100		
3/28/96	118,017	3,690	340	< 100		
4/1/96	349,997	1,422	740	< 100	29	3.2
4/2/96	116,830	1,657	< 100	< 100		

Based on these results, a PF unit was designed and assembled for a full-scale demonstration. The unit used open tubular membranes in the first stage so that solids could be removed simultaneously either with or without the water-soluble

polymer, eliminating the need for bag filters which helped to minimize waste. This first stage was followed by a second smaller stage having a hollow-fiber UF cartridge. We tested several different process conditions such as pH, polymer formulation and polymer contact time. The unit, shown in Figure 12, treated over 1,000 gallons of waste water. Because of these facility constraints the unit was placed at a second waste water treatment facility at LANL, TA-21. This move required further bench-scale testing of the waste water because the influent to this plant was different than at TA-50. A different polymer formulation was developed for this waste stream and we were able to meet our goal of  $< 30\text{pCi/L}$  after process optimization. For one set of data the raw feed had  $1086\text{ pCi/L}$  alpha at pH 7.7. The first tubular UF stage, where no polymer was present in this particular run, gave  $173\text{ pCi/L}$  total alpha in the permeate (simple UF), and the second hollow fiber UF stage (with the water-soluble polymer formulation present) gave  $23\text{ pCi/L}$  total alpha.



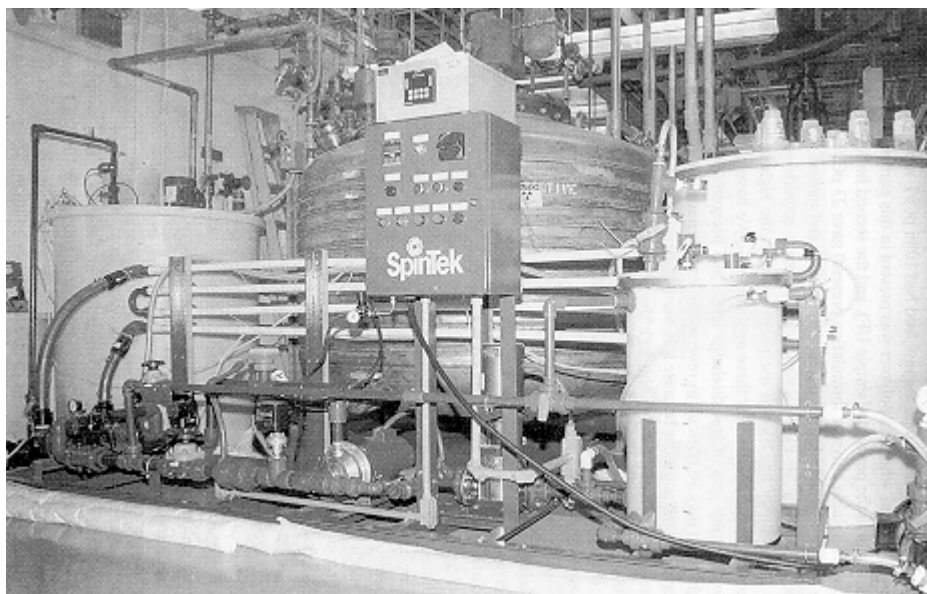
**Figure 12.** Photograph of PF Unit Assembled for a Demonstration to Remove Actinides at a Waste Water Treatment Facility at LANL

In sum, we have tested on the analytical-scale and moved to the bench- and pilot-scale applications of PF on a variety of different actinide-containing aqueous streams. The strategy has been to use polymers with the highest binding constant and not to recycle the polymer for these applications. We have chosen this method in order to attain our goal of low discharge levels and because the binding constants are so high that it may be difficult to reverse the equilibrium. Generally, there is no need to reprocess the actinides because it is more desirable to stabilize the metal for final waste management. Lastly, although the solution activity may

be high, the actual weight of actinide metal is quite small and does not give high loadings on the polymer. If there was a need to recover the metal, redox reactions and competitive chelators would be the likely approaches.

**Electroplating Waste Minimization.** There are over 10,000 electroplating facilities in the United States that discharge an average 55,000 gal/day of waste water that has to meet the regulations of the EPA clean water act. Presently, about 90% of the technology used to meet EPA and state discharge limits involves hydroxide precipitation. This process requires that sludge be contained, shipped, and buried, steps that are costly and constitute industrial liabilities. The metals are valuable and their replacement represents a considerable energy cost. Consequently, in contrast to the approach taken for actinide removal and concentration, it is preferable for the electroplating industry to concentrate, recover, and recycle the metals in-house.

PF technology was first demonstrated at the pilot-scale at Boeing Defense and Space Group in Seattle, WA for nickel-zinc recovery and recycle from new alloy baths under development (7). In all cases, we were able to obtain a permeate that had  $< 0.1$  ppm of nickel and zinc, well below the state and EPA discharge limit. Figure 13 is a photograph of the unit built for the Boeing demonstration. It has a flow diagram similar to Figure 10, but it is a single stage unit. This application is currently being commercialized for general electroplating applications such as zinc, nickel, and copper rinse baths (8).



**Figure 13.** Photograph of PF Unit Built for the Demonstration at Boeing

The summary of the test results taken from a series of baths at the electroplating facility at LANL is shown below in Table II. The samples were

removed from actual electroplating baths and diluted 100 to 1 or 1000 to 1 (based on their original concentration) to represent rinse baths. Metal-Set-Z polymer (8) was added to the pH 7 adjusted solutions to give a 1% w/v solution. The solutions were ultrafiltered (Centricon-10, Amicon) and analyzed by ICP-AES for metal-ion in the permeate. In almost all cases, the permeate was less than 1 ppm metal-ion except where it was apparent we were near the capacity of the polymer (e.g, Cu plate and Ni plate). Thus, not only can the zinc/nickel alloy rinse baths be readily treated, but a series of other electroplating baths including lead, copper, nickel, and zinc can be processed to remove the metal from a variety of different counterions and additives. Further tests using Metal-Set-Z were performed to determine the recovery of metalions that are often found in electroplating baths, either as impurities or as plating metals, from solutions that have chloride, sulfate, or nitrate counterions. Individual solutions containing 0.1 M sulfate, 0.1 M nitrate, and 0.1 M chloride with 0.1% w/v of the polymer were prepared at a pH range of 2 to 7. All solutions contained copper(II), nickel(II), aluminum(III), iron(III), chromium(III), zinc(II), lead(II), and cadmium(II) ions at the 10 to 20 ppm range (low end concentration range expected in electroplating rinse waters). Ten milliliters of the resulting solutions were centrifuged using the Centriprep-10 unit having a MWCO of 10,000 until eight milliliters passed through the membrane. The top (retentate) and bottom (permeate) portions were analyzed by ICP-AES for metal-ion content. The results are summarized below in Tables III and IV.

**Table II.** Results of Treating a Variety of Diluted Electroplating Baths  
With 1% w/v Metal-Set-Z Adjusted to pH 7

<i>Bath Name</i>	<i>Product Name</i>	<i>Composition</i>	<i>Original Bath</i>	<i>Ppm Metal</i>	<i>Dilution Factor</i>	<i>Ppm Metal in Permeate</i>
Cu Strike	M&T Harshaw	CuSO <sub>4</sub> , KOH, Strike Complexer	9	11,070	1/100	0.09
Ni Strike	Made at LANL	NiCl <sub>2</sub> , HCl	<1	72,960 ppm Ni	1/1000	0.43
Bright Ni	Udylite, OMI Int. Corp.	NiSO <sub>4</sub> , NiCl <sub>2</sub> , B(OH) <sub>3</sub> , org. brightener	5	126,100 ppm Ni	1/1000	0.84
Pb Plate	Made at LANL	Pb(BF <sub>4</sub> ) <sub>2</sub> , HBF <sub>4</sub>	<1	284,900 ppm Pb	1/1000	<1
Cu Plate	Udylite, OMI Int. Corp.	CuSO <sub>4</sub> , H <sub>2</sub> SO <sub>4</sub> , HCl, UBAC R-1	<1	71,610 ppm Cu	1/100	1.75
Ni Plate	Made at LANL	NiNSO <sub>3</sub> H, B(OH) <sub>3</sub>	3.5	64,780 ppm Ni	1/100	1.49

Zincate	Made at LANL	ZnO, B(OH) <sub>3</sub>	14	2,595 ppm Zn	1/1000	0.25
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**Table III.** Metal Concentrations in the Permeate with 0.1% w/v Metal-Set-Z in 0.1 M Chloride

<i>pH</i>	<i>ppm</i> <i>Cu(II)</i>	<i>ppm</i> <i>Ni(II)</i>	<i>ppm</i> <i>Al(III)</i>	<i>ppm</i> <i>Fe(III)</i>	<i>ppm</i> <i>Cr(III)</i>	<i>ppm</i> <i>Zn(II)</i>	<i>ppm</i> <i>Pb(II)</i>	<i>ppm</i> <i>Cd(II)</i>
2.00	5.22	14.33	13.03	11.50	11.68	12.73	10.58	12.55
2.87	0.10	14.25	12.58	10.93	12.85	12.85	11.48	12.68
4.03	0.02	2.89	11.63	2.32	7.89	10.94	12.11	10.29
4.78	0.02	0.04	2.19	0.44	0.63	0.63	9.60	0.20
5.94	0.67	0.32	0.31	0.31	0.04	0.14	1.34	0.06

**Table IV.** Metal Concentrations in the Permeate with 0.1% w/v Metal-Set-Z in 0.1 M Nitrate

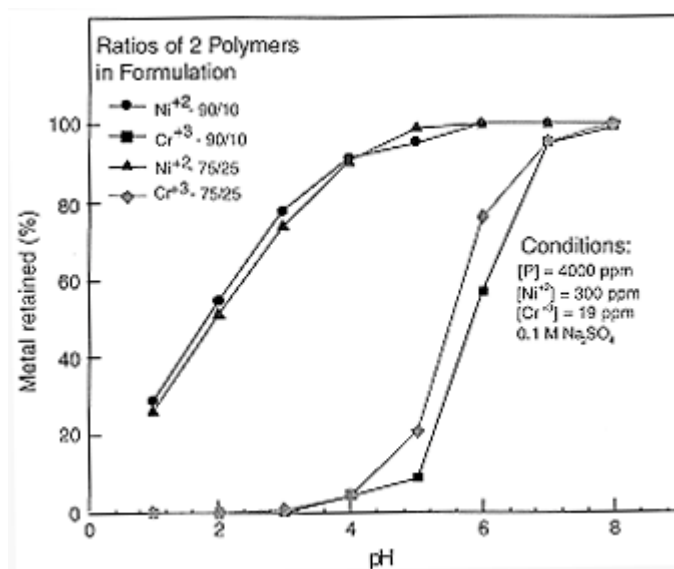
<i>pH</i>	<i>ppm</i> <i>Cu(II)</i>	<i>ppm</i> <i>Ni(II)</i>	<i>ppm</i> <i>Al(III)</i>	<i>ppm</i> <i>Fe(III)</i>	<i>ppm</i> <i>Cr(III)</i>	<i>ppm</i> <i>Zn(II)</i>	<i>ppm</i> <i>Pb(II)</i>	<i>ppm</i> <i>Cd(II)</i>
2.04	3.96	5.19	4.99	3.75	3.71	4.76	2.95	4.31
3.05	0.15	5.16	4.88	2.83	3.47	5.39	2.97	4.28
4.02	0.05	3.72	4.72	0.44	2.67	5.34	2.80	4.36
4.97	0.02	0.04	1.86	0.05	1.73	2.57	2.54	2.70
6.21	0.03	0.02	0.01	0.01	1.15	0.09	0.33	0.04
6.86	0.05	0.02	0.01	0.01	1.49	0.08	0.03	0.05

This polymer was insoluble at < pH 5 in sulfate solutions, but was completely soluble under all other conditions studied. The solubility data demonstrates the importance of knowing the counterions that exist in the waste streams, along with the anion concentration, to be able to choose the proper polymer for the desired separation.

During a beta test of PF at a large electroplating facility in the Midwest, we encountered an interesting situation where chromate was being splattered (unknown to the facility personnel) into the nickel electroplating rinse bath that we were testing. This problem resulted in a performance reduction for the polymer formulation we were testing. Further evaluation indicated that a different



formulation was needed and that some feed adjustment was necessary to convert chromium (VI) to chromium (III). Once that adjustment was made we were able to readily remove both chromium and nickel and selectively recovery the nickel as shown in Figure 14. The two different ratios of polymers tested gave similar results.



**Figure 14.** Chromium(III) and Nickel(II) Retention as a Function of pH

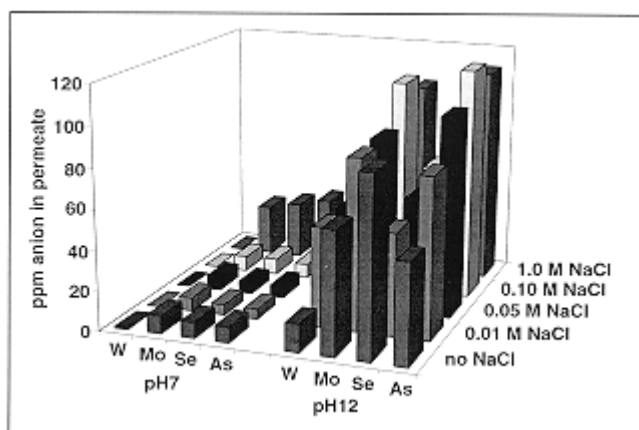
A variety of other polymers, polymer formulations, and electroplating systems have been tested that are too numerous to report here. In several cases other polymers perform better than those reported here, but the cited examples illustrate the utility of the process for general electroplating applications.

**Evaluation of PF for Applications to Oxyanions.** The recovery of oxyanions such as tungstate and chromate is a recurring need in the electroplating industry. Other process or waste streams that contain oxyanions include molybdate from mining wastes, selenate and arsenate from agricultural wastes, and antimonate from manufacturing. Because of their highly soluble nature, these oxyanions can easily enter surface and groundwaters.

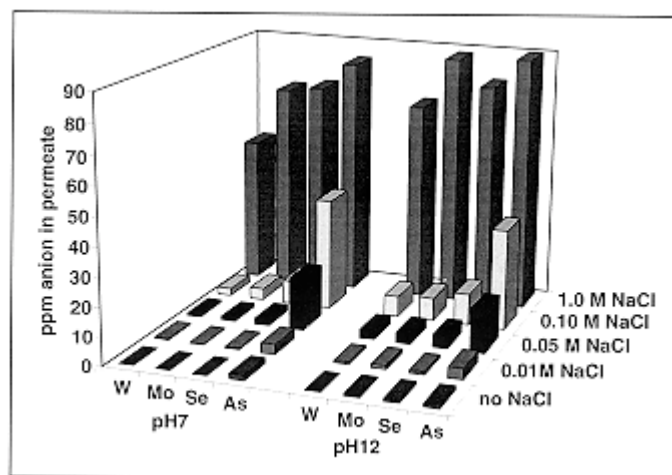
We undertook a survey of oxyanions to evaluate the usefulness of PF for a variety of potential applications. Some previous work on removal of selected oxyanions from aqueous streams using water-soluble anion exchangers has been reported (9). Our study was intended as a baseline to determine if further polymer development was necessary.

The first approach was to evaluate the effect of simple weak and strong base anion exchangers and determine their retention ability under a variety of

competing salt conditions and several different pH values. These were performed by preparing 100 ppm solutions of the respective oxyanion at the proper pH value and contacting them with a solution of the water-soluble anion exchange polymer to give a final 1% w/v concentration of the polymer. The solutions were mixed, filtered through a Centricon-10 unit, and the permeate analyzed for the oxyanion using ion chromatography (Dionex). Figures 15 and 16 show the results at pH 7 and 12 in the presence of increasing NaCl concentration. Experiments were not performed at lower pH values as some oxyacids precipitate from solution.



**Figure 15.** Plots of Permeate versus pH and Salt Concentration for a Variety of Oxyanions Using a 1% w/v Weak Base Anion Exchanger



**Figure 16.** Plots of Permeate versus pH and Salt Concentration for a Variety of Oxyanions Using a 1% w/v Strong Base Anion Exchanger

It is apparent that retention decreases for all anions at higher salt concentrations for both the strong and weak anion exchangers. At higher pH, the weak anion exchanger does not bind well compared to the strong anion exchanger



as is expected when the ammonium ion exchange sites are deprotonated. Molybdate, tungstate, and selenate showed the highest overall retention with a permeate concentration of  $< 0.5$  ppm under 0.01 M sodium chloride conditions with the strong base anion exchanger and almost ten times that amount for the weak base anion exchanger under the same conditions. Arsenate gave poor results under the experimental conditions with the best removal of 3.4 ppm under 0.01 M NaCl conditions. Arsenate binding is poor because it is not fully deprotonated to the dianionic species until pH 8.5. Though feed adjustment to pH 8.5 may be desirable for process waste waters, for drinking water treatment it would be less desirable to require chemical adjustment to optimize arsenic removal.

From our results, it can be seen that there are many situations where dilute salt solutions could be readily treated to remove oxyanions using simple anion exchange polymers. One of those dilute solution systems would be from groundwater, and chromium removal has been reported using a strong base anion exchanger (19). In those situations where there are high salt concentrations or greater selectivity is needed, other polymers will be required.

**Recovery of Metals from Acid Mine Drainage: Treatment of Berkeley Pit Waters (BPW).** Water flows into the Berkeley Pit in Butte, Montana, (Figure 17) with a volume of approximately 20 billion gallons from runoff and underground water sources at  $>3500$  gallons per minute. Acidic water produced from bacterial action on the sulfide ores leaches toxic levels of metal-ions from the surrounding mining district in the form of sulfates causing the water to have a pH of about 2.6. It is anticipated that the pit will reach capacity by approximately the year 2015 (21), and treatment is required to prevent water from entering the local rivers and aquifers. The current baseline technology for treatment of the BPW is precipitation of all metals with lime such that the liquid discharge meets criteria for discharge into a POTW or into the local rivers, and that the sludge resulting from precipitation will be buried in the original mine tailings or accumulate on the pit bottom (22). In this way, no metal value is recovered and only the overflow issue is addressed. Precipitation does not address the issue of excess sulfate in the waters, nor does it assure that fresh acid leach water will not redissolve the metals from the hydroxide/carbonate precipitate in the future.



**Figure 17.** Photograph of the Berkeley Pit in Butte, MT

In the estimated 20 billion gallons of contaminated water in the Berkeley Pit there are 61 kilotons of copper and 176 kilotons of zinc. In most of the western states there are thousands of abandoned mine sites of which 10% are thought to have a problem with acid mine drainage. In addition, there are many active mine sites that require management of water and acid drainage.

We have completed a preliminary proof-of-principle evaluation of PF technology for removal of hazardous metal-ions and recovery of valuable metal-ions from BPW. In concert with several other separations technologies, PF can both remove nuisance metals such as aluminum and iron and recover valuable metal such as copper and zinc while removing other hazardous trace metals such as lead and chromium. A water stream suitable to be added to the local streams or used for irrigation could result.

Our strategy for solving the BPW problem is based on the fact that there are large amounts of aluminum and iron present that need to be separated from the more valuable and hazardous metals. Non-hazardous metals, such as calcium, potassium, and sodium, can be discharged with the water. It is uncertain if aluminum and iron have any value at this time, but it might be desirable to remove them separately. The main metals of value in large amounts are copper and zinc. Only small amounts of nickel are present. Table V gives the analytical composition of BPW averaged over three depths.

**Table V.** Composite Composition from Three Depths of Acid Mine Drainage Water\* from the Berkeley Pit, Butte, Montana

Element (ppm)	Element (ppm)	Element (ppm)
Ca(478)	B (0.40)	V (0.11)
Mg (418)	Cd (1.67)	Zn (528)
Na (69)	Cu (184)	As (0.53)
K (18)	Li (0.26)	Co (1.75)
SiO <sub>2</sub> (97.5)	Mo (0.058)	Cr (0.055)
Fe (875)	Ni (1.06)	Cl (12)
Mn (186)	Sr (1.36)	SO <sub>4</sub> (7643)

\* pH = 2.6

To increase the efficiency of the PF process we felt it would be advantageous to initially remove as much of the iron and aluminum from the water as possible. If left in the waters, their high concentrations would potentially deplete the polymer's metal-binding capacity, necessitating higher polymer concentration. Additionally, if any electrochemical recovery approaches are used, iron is a major interference because it is quite electroreactive. For optimum metal-ion-binding of the polymers used in our experiments, it is necessary that the pH be raised to approach neutral values (ultimately for discharge to POTW the waters must be nearly neutral).

The addition of hydroxide (i.e., as potassium hydroxide or sodium hydroxide, etc.) presents a number of problems. As the pH is raised, iron and aluminum will slowly precipitate from solution. The precipitation of metal hydroxides can result in the inclusion of large amounts of other metals (e.g., copper, and zinc) within the iron and aluminum hydroxides generating complex mixtures of metals.

We decided to take advantage of one of the water-soluble polymer's chelating abilities, in addition to its basicity, to eliminate the disadvantages of hydroxide precipitation. By adding sufficient polymer to complex all the metal-ions except iron and aluminum, we anticipated that copper, zinc, and other metals in solution would remain bound as polymer-metal complexes, selectively precipitating the iron and aluminum (solubility at pH 4.8; Al(III) = 0.1 ppm, Fe(III) = 0.001 ppm).

A general procedure involved treating the BPW with a dilute solution of basic polymer to adjust the pH of the water to near 4.8. The solid precipitate was separated by centrifugation. The pH of the supernatant was then increased so that most of the valuable and toxic metal-ions became completely polymer bound. The supernatant was ultrafiltered to concentrate the metal-ions and to give a permeate free of hazardous metals for discharge (after sulfate and manganese are removed).

The first test involved treating BPW (20 mL) with dilute polymer solution (2 mL, 50,000 ppm of polymer) to adjust the pH of the water to pH 4.8. It was noted that upon the addition of the polymer solution, the pH of the water increased and immediately stabilized at 4.9 resulting in rapid and nearly complete iron and aluminum precipitation. The supernatant was separated from the solid by centrifugation and allowed to sit overnight. No additional precipitate was observed and the pH changed by no more than 0.1 units. This result is evidence of the rapid kinetics of the precipitation process. The procedure was repeated a number of times and was reproducible. Table VI gives typical metal-ion concentrations found in the supernatant in comparison to the metal concentrations found in 20 mL of raw BPW. The analysis indicated all the iron and 95% of the aluminum was removed from solution with zinc (100%), magnesium (100%), manganese (98%), and copper (72%) remaining in solution. A water wash of the precipitate yielded another 10% of copper bringing the recovery to 82%. We thought that a continuous wash step would recover more of the polymer-copper complex from the iron/aluminum sludge. The above experiment was repeated on 80 mL of BPW using 10 mL of polymer solution with similar results. This approach might indicate that the process can be readily scaled.

Previous work (see Tables III and IV) has shown that we can selectively separate the zinc from the copper by simple pH adjustment once the majority of the iron and aluminum is removed from solution. The polymer forms a less stable complex with zinc, allowing it to be selectively stripped from the polymer at a higher pH value. Once the zinc is collected in a concentrated solution, the copper can also be removed from the polymer as a concentrated solution. Although these results were encouraging, we need to emphasize that the process has not been optimized.

**Table VI.** Metal Content (ppm) of Berkeley Pit Water After Various Treatments

<i>Element</i>	<i>Untreated Sample pH 2.6<sup>a</sup></i>	<i>After NaOH pH 3.0<sup>b</sup></i>	<i>After KOH pH 3.8<sup>b</sup></i>	<i>After NH<sub>4</sub>OH pH 3.8<sup>b</sup></i>	<i>After Metal- Set-Z pH 4.8<sup>b</sup></i>	<i>After Metal- Set-C pH 5.6<sup>c</sup></i>
Fe	17.21	4.47 (26%)	2.97 (17%)	0.02 (<1%)	0.0 (<1%)	< 0.01
Mn	3.99	---	---	---	4.12 (103%)	---
Al	5.92	4.51 (76%)	4.29 (72%)	3.64 (62%)	0.31 (5%)	< 0.01
Cu	3.74	3.33 (89%)	3.25 (87%)	3.04 (81%)	3.04 (81%)	< 0.01
Mg	8.82	---	---	---	8.7 (98%)	---
Zn	10.74	10.95 (103%)	10.8 (100%)	9.82 (92%)	11.2 (104%)	< 0.01

<sup>a</sup> Values are the amount in mg of each metal in 20 mL of BPW.

<sup>b</sup> Values are reported as mg of metal remaining in solution after precipitation from 20 mL of BPW. Values in parentheses are the percent of metal remaining in solution based on original BPW. Metal-Set-Z, PolyIonix, Dayton, NJ.

<sup>c</sup> Sample from NaOH precipitation treated with 0.12% w/v Metal-Set-C, PolyIonix, Dayton, NJ.

To show PF effectiveness in meeting metal-ion discharge levels after the precipitation of iron and aluminum, the BPW (20 mL) was treated in a similar manner as above with a different polymer, Metal-Set-C, resulting in a final pH of 5.6. The supernatant was removed from the iron/aluminum precipitate and ultrafiltered through a 10,000 MWCO membrane. Analysis of the permeate discharge waters by ICP-AES indicated metal concentrations below detectable limits for copper, aluminum, iron, and zinc of <0.01 ppm and nickel, chromium, lead, and cadmium of <0.3 ppm. The preliminary evaluation of PF as a technology for the recovery of metal-ions from the Berkeley Pit has proven to be very encouraging.

We have successfully shown that the addition of the appropriate amount of a basic water-soluble polymer to the untreated water results in the selective precipitation of iron and aluminum from the copper, zinc, and manganese by a kinetically rapid process. This process has the potential advantage of an in-line treatment as compared with a batch-type process. It has been shown in previous work that the zinc and copper can be separated selectively by pH adjustment. The

polymers are recycled in the system for additional metal-ion recovery; therefore, a secondary waste stream is not generated. Analysis of discharge or permeate waters were below detectable levels of metals which demonstrates the effectiveness of PF as a polishing step for low-level concentrations of metals.

## **Summary**

The PF system is a technology for removing, concentrating, and recycling metal-ions from industrial waste water, thereby conserving valuable resources and reducing pollution. In its current commercial application for the electroplating industry, the system can be sized for both large and small operations. PF is a new process that will see broad application in industry. The following applications are under investigation in our laboratory:

- (1) Analytical preconcentration,
- (2) Nuclear power/nuclear facility waste streams,
- (3) Electroplating rinse waters,
- (4) Photofinishing waste streams,
- (5) Acid Mine drainage/advanced mining techniques,
- (6) Treatment of ground water/drinking water,
- (7) Precious metals industry,
- (8) Catalyst waste streams,
- (9) Electronics waste streams,
- (10) Cooling tower water,
- (11) Textile waste streams,
- (12) Municipal waste streams,
- (13) Soil remediation/surface decontamination.

Polymer Filtration is a technology worthy of consideration in any situation where dilute waste stream polishing or dilute metal-ion recovery is needed.

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